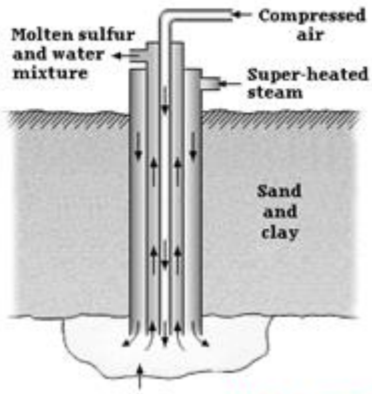
CHEM 9.5.3 SULFURIC ACID

Sulfuric acid is one of the most important industrial chemicals

3.1 Outline **three uses** of sulfuric acid **in industry**

- **Fertiliser**
  - **Superphosphate fertiliser** (calcium sulfates (insoluble) and calcium dihydrogen phospates)
  - **Ammonium sulfate**: $H_2SO_{4\,(aq)} + 2NH_{3\,(aq)} \rightarrow (NH_4)_2SO_{4\,(aq)}$
- **Steel processing/pickling**
  - Remove **surface rust** (iron oxide) and grease/dirt from **steel** before galvanising/coating
- **Dehydrating agent**
  - Concentrated H_2SO_4 used in producing **ethylene from ethanol**
    - Water removed: $C_2H_5OH_{(l)} \xrightarrow{H_2SO_4} C_2H_{4\,(g)} + H_2O_{(l)}$
  - Also for drying chlorine gas for explosives, dyes

3.2 Describe the processes used to **extract sulfur** from mineral deposits, identifying the **properties of sulfur** which allow its extraction and analysing potential **environmental issues** that may be associated with its extraction



- Sulfur from mineral deposits found in **elemental form**
- Extracted through **Frasch process:**
  - Three concentric pipes to sulfur
    - **Superheated water** (**160°C**) outer, melts sulfur
    - **Liquid sulfur and water** middle, S separates when solid
    - **Compressed air** inner, pushes emulsion up
- Also can be extracted from **hydrogen sulfide** in natural gas/petroleum
  - Incomplete combustion of H_2S
  - $4H_2S_{(g)} + O_{2\,(g)} \rightarrow 2H_2S_{(g)} + \mathbf{S}_{(s)} + SO_{2\,(g)} + 2H_{2\,(g)}$
  - $2H_2S_{(g)} + SO_{2\,(g)} \rightarrow 2H_2O_{(g)} + 3S_{(g)}$: mixture is condensed
- **Properties** of sulfur allowing Frasch process:
  - **Low MP** (113°C – water melts sulfur)
  - **Low density** (foamy mixture with water easily lifted up)
  - **Insoluble in water** so extracting only requires cooling (99.5% S)
- **Issues** with extraction:
  - Easily **oxidised to SO_2** or **reduced to H_2S** – air pollutants at low concentrations – acid rain
  - Water may **dissolve impurities** and may be contaminated – water should be reused
  - Water may cause **thermal pollution** to environment
  - **Earth subsidences (**difficult to refill cavern, may collapse)

3.3 Outline the **steps and conditions** necessary for the **industrial production of H_2SO_4** from its raw materials

- Raw materials – **sulfur, oxygen and water**
- **3 steps** – called Contact process

SULFUR TO **SULFUR DIOXIDE**

$$S_{(s)} + O_{2\,(g)} \rightarrow SO_{2\,(g)}$$

- **Molten sulfur sprayed** into furnace with air that has been **dried** (with excess oxygen) in **combustion furnace**
- Sulfur dioxide also from metal refineries, e.g. $2ZNS_{(s)} + 3O_{2\,(g)} \rightarrow 2ZnO_{(s)} + 2SO_{2\,(g)}$

SULFUR DIOXIDE TO **SULFUR TRIOXIDE**

$$2SO_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2SO_{3\,(g)}\ \Delta H = -99\text{kJ/mol}$$

- Sulfur dioxide fed into a **conversion tower**, converting it into sulfur trioxide through **catalytic oxidation**
- Pressure **1 atm**, excess of **oxygen**, **400-550°C**, catalyst **vanadium(V) pentaoxide V_2O_5** on porous **silica pellets**
- Goes through once at 550°C, then twice at 400°C to **ensure maximum SO_2 converted** – 99.7%

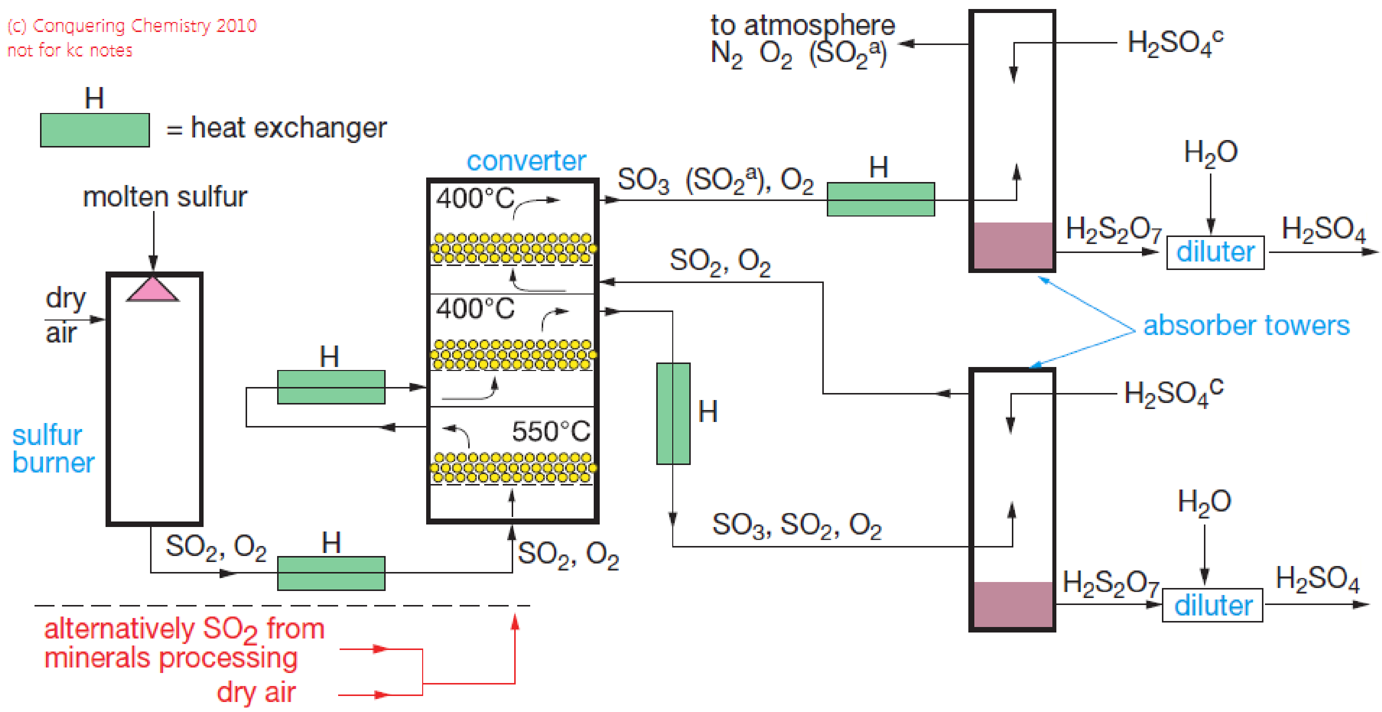
SULFUR TRIOXIDE TO (**OLEUM**) TO **SULFURIC ACID**

$$SO_{3\,(g)} + H_2O_{(l)} \rightarrow H_2SO_{4\,(l)}$$

- Above reaction is **very exothermic** and **H_2SO_4 becomes a mist** – too expensive to separate from gas
- Sulfur trioxide therefore dissolved into concentrated sulfuric acid to form **oleum $H_2S_2O_7$**:

$$SO_{3\,(g)} + H_2SO_{4\,(l)} \rightarrow H_2S_2O_{7\,(l)}\ \text{then}\ H_2S_2O_{7\,(l)} + H_2O_{(l)} \rightarrow 2H_2SO_{4\,(l)}$$

- Produces 98% H_2SO_4



3.4 Describe the **reaction conditions** necessary for the **production of SO_2 and SO_3**

PRODUCTION OF SO_2

- $S_{(s)} + O_{2\,(g)} \rightarrow SO_{2\,(g)} + \text{heat}$
  - Oxidation of sulfur done in a **combustion furnace** and goes to completion
  - Molten sulfur sprayed into **dry, oxygen-rich** air

PRODUCTION OF SO_3

- $2SO_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2SO_{3\,(g)} + \text{heat}\ \Delta H = -99\text{kJ/mol}$
  - Oxidation of sulfur dioxide is **reversible and reaches equilibrium**
  - Reaction in **conversion tower** with **vanadium(V) pentaoxide** V_2O_5 on porous silica pellets as catalyst
    1. SO_2 and O_2 cooled to **550°C**, and passed through catalyst – **70%** conversion (higher rate)
    2. SO_2 and O_2 cooled to **400°C**, and passed through catalyst – **97%** conversion (higher yield)
    3. **SO_3 is removed**, remaining SO_2 and O_2 cooled to **400°C** and passed through catalyst – **99.7%**
  - Residue gas released into atmosphere

3.5 Apply the relationship between **rates of reaction and equilibrium conditions** to the **production of SO_2 and SO_3**

PRODUCTION OF SO_2

- Sulfur should be **liquid and sprayed** to increase **surface area** to increase **reaction rate**
- No equilibrium considerations required

PRODUCTION OF SO_3

- $2SO_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2SO_{3\,(g)} + \text{heat}\ (\Delta H = -99\text{kJ/mol})$
- **Reaction rates** increased by:
  - **High temperatures** – more molecular collisions
  - **Catalyst** – Vanadium(V) oxide lowers **activation energy**
- **Yield increased** according to Le Chatelier's Principle:
  - **Lower temperatures** – favours products
  - **Higher pressure** – as there are less moles of gas produced
  - **Excess of oxygen** – shifts equilibrium to right
- **Compromise**:
  - **400°C** to **500°C**, pressure at 1 atm reduces costs

3.6 Describe, using examples, the **reactions of sulfuric acid** acting as:

AN **OXIDISING** AGENT

- **Oxidising agent (oxidant) becomes reduced** – it brings about oxidation
  - H_2SO_4 therefore gains electrons (OIL**RIG**)
  - Half equation for sulfuric acid is $\boldsymbol{H_2SO_{4\,(aq)} + 2H^+_{(aq)} + 2e^- \rightarrow SO_{2\,(g)} + 2H_2O_{(l)}}$
- For example **copper** (unreactive metal) becomes **oxidised** to form **copper sulfate, sulfur dioxide and water**
  - $Cu_{(s)} + 2H_2SO_{4\,(aq)} \rightarrow CuSO_{4\,(aq)} + SO_{2\,(g)} + 2H_2O_{(l)}$ where **one SO_4 is a spectator ion**
  - Therefore half equation is $Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$
- **Iodide and bromide ions** oxidise to form iodine and bromine
  - $2I^-_{(aq)} + 3H_2SO_{4\,(aq)} \rightarrow I_{2\,(aq)} + SO_{2\,(aq)} + 2H_2O_{(l)} + 2HSO^-_{4\,(aq)}$ half equation $2I^-_{(aq)} \rightarrow I_2 + 2e^-$

A **DEHYDRATING** AGENT

- Sulfuric acid has **strong affinity** – and absorbs water from mixtures
- Sulfuric acid **dehydrates sucrose** to create **carbon** (spongy) and **water**
    - $C_{12}H_{22}O_{11\,(s)} \xrightarrow{H_2SO_4} 12C_{(s)} + 11H_2O_{(l)}$
- Similarly, used for **esterification** and removing **water from alkanols**

3.7 Describe and explain the exothermic nature of sulfuric acid ionisation

- Sulfuric acid ionises in water into H^+, HSO_4^- and SO_4^{2-} ions, in **two steps**
- **First dissociation**: $\mathrm{H_2SO_{4\,(aq)} + H_2O_{(l)} \rightarrow HSO_{4\,(aq)}^- + H_3O^+ + heat\ (\Delta H = -90kJ/mol)}$
    - H^+ combining with water form H_3O^+ ions
    - This energy releases much greater than energy than breaking bonds of H_2SO_4
    - Therefore ionisation is strongly exothermic
- **Second dissociation**: $HSO_{4\,(aq)}^- + H_2O_{(l)} \rightleftharpoons SO_{4\,(aq)}^{2-}$
    - Only occurs slightly, negligible ($K = 1.2 \times 10^{-2}$)

3.8 Identify and describe **safety precautions** that must be taken when **using and diluting** concentrated sulfuric acid

- Concentrated sulfuric acid – 98% H_2SO_4 (very few ions)
- Wear **protective gloves and a laboratory coat** (corrosive to skin and clothing), **safety goggles** (splash to eye)
- Do not allow water to enter bottle – water will boil violently, may crack container
- Add **small amounts of acid to water** with constant **stirring** when diluting
    - Allows heat to disperse and prevents water from boiling
- Clean spills with **sodium carbonate or sodium hydrogen carbonate**

3.P1 Gather, process and present information from secondary sources to describe the **steps and chemistry involved** in the **industrial production of H_2SO_4** and use available evidence to analyse the process to predict ways in which the **output of sulfuric acid can be maximised**

- Industrial production of H_2SO_4 steps and chemistry: 3.3
- Prediction of maximising output: 3.3, 3.4, 3.5

3.P2 Perform first-hand investigations to **observe the reactions** of sulfuric acid acting as:

AN **OXIDISING AGENT**

- A **zinc granule** placed into a test tube and **3 mL 2 mol H_2SO_4** added
- **Bubbles formed** indicating gas formed: $Zn_{(s)} + 2H_3O_{(aq)} \rightarrow Zn^{2+} + \boldsymbol{H_{2\,(g)}} + 2H_2O_{(l)}$

A **DEHYDRATING AGENT**

- In a **fume cupboard**, 10 mL H_2SO_4 added to beaker with 50 grams sucrose and stirred
- Sugar became black and began to smoke (steam), foamy black carbon was created:
    - $C_{12}H_{22}O_{11\,(s)} \xrightarrow{H_2SO_4} 12C_{(s)} + 11H_2O_{(l)}$

3.P3 Use available evidence to relate the **properties of sulfuric acid** to **safety precautions** necessary for its **transport and storage**

- **Concentrated H_2SO_4** does not react with **iron or steel** (H^+ ions cause reaction and form H_2 gas)
  - Can be stored and transported in steel tanks, **preferred over glass or plastic**
- **Dilute H_2SO_4** will react with container, so **glass and plastic containers** used (more expensive)
- **Moisture** (from air) should be removed, container shut, as it can cause vigorous reaction
- When storing:
  - Place bottle in **drip tray** (beaker/Petri dish) so drips do not touch shelf/bench
  - Store in **glass or plastic bottles** if dilute
  - Lid should be **shut** to prevent absorbing water from air
- This is because sulfuric acid:
  - **Dehydrating agent** and can damage organic material
  - **Strong acid** that can corrode and damage metals
  - **When ionisation occurs**, reaction is very exothermic and can break/melt container